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Determination of Halogenated Acetic Acids by Ion Chromatography

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Adsorption of toxic gases on the surfaces of various synthetic and natural tubing is a critical factor when the tubing is used for sampling purposes. The affinity of the tubing's surface for toxic gases may be either reversible or irreversible, i.e., the toxic gases may be involved in some type of chemical reaction with the tubing or with another previously adsorbed material, or gases may be reversibly adsorbed. This research explores the adsorption characteristics of toxic gases on the surfaces of tubing commonly used in the laboratory. The tubing used in this study was connected to the inlet port of a real-time gas monitor. At the start of the run, a known concentration of gas, generated with a toxic gas diluter, was introduced into the sample tubing at a flow rate of 5 L/min. We measured the time it took for the gas to flow through the tubing and be detected by the gas monitor. By comparing the delay time measured by the chart recorder with the theoretical delay time associated with zero adsorption, one could estimate the relative amounts of adsorption. A known concentration of gas was allowed to continuously pass

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through the tubing until the monitor's response and the diluter were within 10 percent agreement. The toxic gas flow from the diluter was then stopped as the desorption time was measured as the system slowly returned to zero adsorption. Although this study has been limited to hydrogen chloride, these preliminary findings do suggest that adsorption effects of various tubing should be considered a potential source of error when sampling and quantitatively measuring toxic gases. Recent work on the adsorption characteristics of toxics gases on several commercial tubing will be discussed.

DISCLAIMERS

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INTRODUCTION

The purpose of this investigation was to develop a specific, highly sensitive, reproducible ion chromatographic (IC) method for the detection of monofluoroacetic acid (MFA), chloroacetic acid (CAA), bromoacetic acid (BAA), iodoacetic acid, and sodium acetate.

Monofluoroacetic acid is an intensely poisonous rodenticide and predacide. Because of its extreme toxicity, MFA is not favored as a general pesticide. Several reports have been made of incidents where MFA had been used to maliciously poison nontarget animals (1). Moreover, the Army considers MFA as an opportunity poison, and its potential for contaminating field drinking water is of great concern.

There have been several published methods for the determination of MFA using gas chromatography or gas chromatography/mass spectrometry (2-5), thin layer chromatography (6), and liquid chromatography (7,8). However, all these methods have one problem in common--they involve time-consuming sample preparation which makes them unsuitable for rapid analysis. Therefore, a reliable analytical method was needed to determine the effectiveness of the Army's in-house reverse osmosis water purification unit (ROWPU) for removing these halogenated acetic acids from typical field water supplies.

EXPERIMENTAL

EQUIPMENT. Ion chromatography was done using a Model 4000i ion chromatograph (Dionex Corporation, Sunnyvale, CA) equipped with a gradient pump, conductivity cell, autosampler (Model ASM-2), eluent degas system, and anion micromembrane supressor. A Dionex AutoIon 450 Chromatography Automation System, connected to an IBM computer, was used to measure peak areas, identify retention times, and store data. The analytical columns used for isocratic inorganic anion and organic acid determinations were the IonPac AS5A-5 microcron with corresponding guard column and the IonPac ICE-AS1 column, respectively. A 0.2-mL sample loop was used with both columns. The eluent for the anion column was 0.0039 M sodium bicarbonate and 0.0031 M sodium carbonate, flowing at 1.0 mL/min. The eluent used with the organic acid column was 1 mM octanesulfonic acid in 2 percent propanol. The eluent flow rate was 0.8 mL/min. The suppressant solution used for the anion and the organic acid column were 0.025 N sulfuric acid and 5 mM tetrabutylammonium hydroxide (TBAOH), respectively. All analyses were performed at room temperature.

REAGENTS AND MATERIALS. All chemicals used were of reagent-grade quality. Tetrabutylammonium hydroxide (TBAOH) 55 percent solution was obtained from Southwestern Analytical (Austin, Texas 78704). Sulfuric acid and HPLC-grade 2-propanol were purchased from Fisher Scientific (Pittsburgh, PA 15219). The sodium salts of the halogenated acetic acids and sodium acetate were purchased from Aldrich Chemical (Milwaukee, Wisconsin 53233). HPLC-grade 1-octanesulfonic acid sodium salt was purchased from Eastman Kodak (Rochester, NY 14650). Deionized water for the IC was obtained by passing distilled water through a Millipore water purification system (Bedford, MA 01730). All standards were made with ROWPU feed water spiked with the contaminant.

ELUENT PREPARATION. The anion eluent was a solution of 0.0039 M sodium bicarbonate and 0.0031 M sodium carbonate. An 0.1 M concentrated stock solution of the eluent was prepared by weighing out approximately 8.4 g of sodium bicarbonate and 10.6 g of sodium carbonate and dissolving each into 1 L of deionized water. Both stock solutions were stored in a refrigerator at $4^{o}C$. Seventy-eight mL of the 0.1 M sodium bicarbonate and 62 mL of the 0.1 M sodium carbonate were dispensed into a 2,000-mL volumetric flask which had been partially filled with deionized water. The solution was brought to its final volume by adding more deionized water.

The regenerant used as the suppressant for the anion suppressor was a solution of 0.025 N sulfuric acid. The regenerant was prepared in a 5-gal plastic bottle, partially filled with deionized water, by carefully dispensing 14 mL of concentrated sulfuric acid and diluting up to 20 L. This solution was stored at room temperature and dispensed as needed.

Octanesulfonic acid (1 mM) in 2 percent 2-propanol was the eluent used with the organic acid column. This was prepared by dispensing 40 mL of 2-propanol into a 2,000-mL volumetric flask in approximately 500 mL of deionized water. One octanesulfonic acid sodium salt (0.432 g) was added to the solution, mixed thoroughly to dissolve, and brought to a final volume with deionized water. Both the anion eluent and the eluent used with the organic acid column were degassed and stored under helium.

TBAOH was the regenerant for the organic acid membrane suppressor. A 5 mM TBAOH solution was prepared from 55 percent TBAOH by dispensing 10 mL into the regenerant reservoir and diluting with deionized water to the 4-liter mark.

PREPARATION OF STOCK AND STANDARDS. The U.S. Army Toxic and Hazardous Materials Agency (USATHAMA) Quality Assurance Program (9) was used as a guide for preparing certification and calibration standards. The calibration master stock was used to prepare daily calibration standards. Sample spikes used in all certification analyses were prepared at each concentration from the certification master stock solution. In both cases, the stock solutions were prepared separately and independently by dissolving the appropriate weighed amount of each acid into a 500-mL volumetric flask to make a 1,000 ppm stock solution. For certification, USATHAMA's repartition involved a series of standards spiked in the concentration series 0 X (method blank), 0.5 X, 1 X, 2 X, 5 X, and 10 X, where X is the concentration of the analyte that corresponds to the reporting limit. Because the actual value for X was not known prior to preparing the standard series, the value of X was arbitrarily chosen to be 10 ppm.

SAMPLE PREPARATION. The autosampler vials were marked with the appropriate identification numbers. A microliter pipet was used to transfer the standards into a 0.5 mL autosampler (polyethylene) vial. A black filter cap was inserted into each vial until it was flush with the top of the vial. Any excess fluid was wiped away to avoid contamination from other samples. After all trays were filled, they were properly aligned in the autosampler.

RESULTS

The halogenated acids of interest included bromoacetic acid, chloroacetic acid, monofluoroacetic acid, iodoacetic acid, and sodium acetate. An ion chromatography method could not be developed to detect iodoacetic acid; therefore, it was excluded from this study.

All halogenated acids used in this study were purchased as sodium salts. Because they were considered ionizable salts, their presence in ROWPU water samples could be determined using Dionex isocratic separation procedures for organic anions. All components in the matrix could be resolved in 8 min. An isocratic inorganic anion chromatogram of a ROWPU water sample spiked with MFA is shown in Figure 1. The retention time of the MFA is approximately 1.32 minutes. The retention times for the other halogenated acids are given in Table I. Because these halogenated acids elute before 2.0 min, it would be difficult to resolve them from a matrix spiked with fluoride and formate. In some cases, the chloride normally present in the feed water sample coeluted with chloroacetic acid and bromoacetic acid thus making it difficult to resolve the peaks above 75 ppm.

A chromatogram obtained for the halogenated acetic acids using the ICE method are given in Figure 2. The retention times for the halogenated acetic acids using the ICE technique are given in Table I. There was virtually no interference or coelution of other species. The halogenated acetic acids are well resolved from the inorganic anion peaks and elute in approximately 15 min.

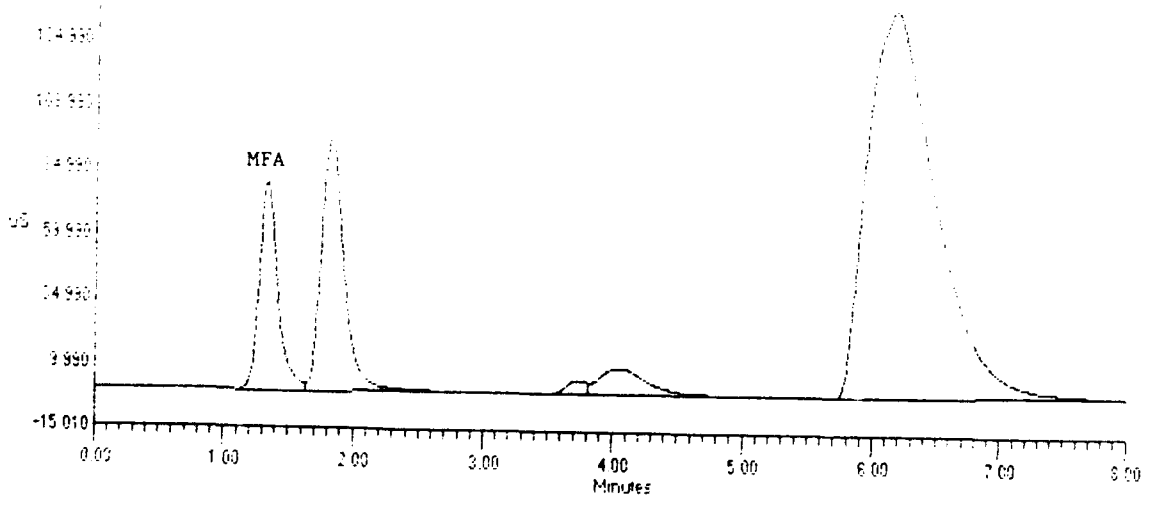

Figure 1. Isocratic inorganic anion chromatogram of a ROWPU water sample spiked with 50 ppm MFA.

Table I. Retention Times for Halogenated Acetic Acids

Halogenated Acetic Acid	Retention Time, min	
	Columns	
	AS5A-5	ICE-AS1
BAA	1.63	10.78
CAA	1.52	9.40
MFA	1.32	8.05
ACETATE	1.28	12.72

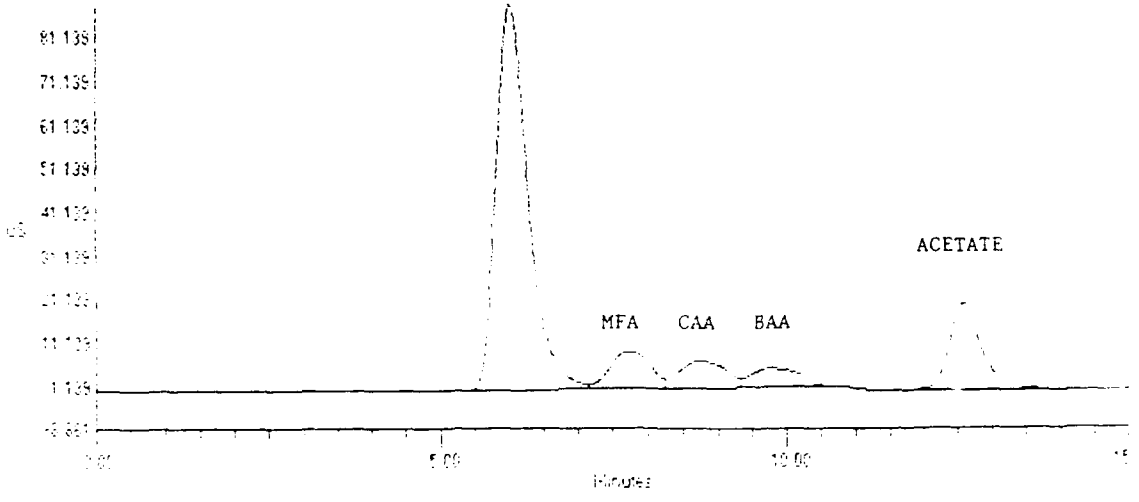

Figure 2. Typical chromatogram of ROWPU water sample spiked with 50 ppm of MFA, CAA, BAA, and acetate.

USATHAMA's quality assurance program was used to handle the calibration and certification data generated from both methods. The reproducibility of the measurements was determined by making three replicate measurements at each target concentration. The prepared standards where introduced into the IC to obtain the corresponding instrument area count responses for the calibration curve. All calibration curve data were subjected to least-squares linear regression analysis. In all cases the correlation coefficient was greater than 0.998.

For method certification, found concentrations were generated by the computer by internally entering the response values into the calibration curve and computing the corresponding concentrations. USATHAMA's program utilizes the information generated by the computer to directly convert the found concentrations into a standard deviation value for each target concentration response. An example of some of the statistical data generated by the program for MFA is given in Table II. In addition to the statistical data, the program plots the spiked target concentrations and their corresponding found concentrations for the entire data set (Figure 3). From this particular data set, one can observe from this graph the linearity in the method responses through the range of interest.

Table II. Ion Chromatographic Method Calibration Curve Calculations for MFA on the Anion Column

Prepared Conc. (ppm)	Experimental Area Count	Found Conc. (ppm)	Standard Deviation
5.00	80809	5.12	0.157
	77219	4.89	
	76065	4.81	
10.0	155142	9.85	0.040
	154607	9.82	
	155866	9.90	
20.0	309829	19.71	0.285
	301185	19.16	
	303388	19.30	
50.0	783277	49.89	0.933
	799042	50.89	
	812527	51.75	
100	1585813	101.04	0.459
	1588160	101.19	
	1599295	101.89	

The USATHAMA's program estimates a certified reporting limit (CRL). It is important to note that when using USATHAMA's program for computing CRLs, one should prepare all spiked samples equidistant from one another and demonstrate linearity through the analytical method. In all cases the target reporting limits, arbitrarily chosen prior to the analysis, were much higher than the calculated CRL values (Table 3). The CRL for those acids resolved on the anion column corresponded with the instrument's detection limit for that column. However, the CRL calculated for the organic acid column were significantly lower than what the instrument could actually detect. Despite the good overall fit of the calibration data, the reason for this discrepancy

is not known. However, USATHAMA suggests that the found concentration calculations and the detection limits could possibly be improved by extending the range of the data set to include more lower values. This approach was not used in the present investigation.

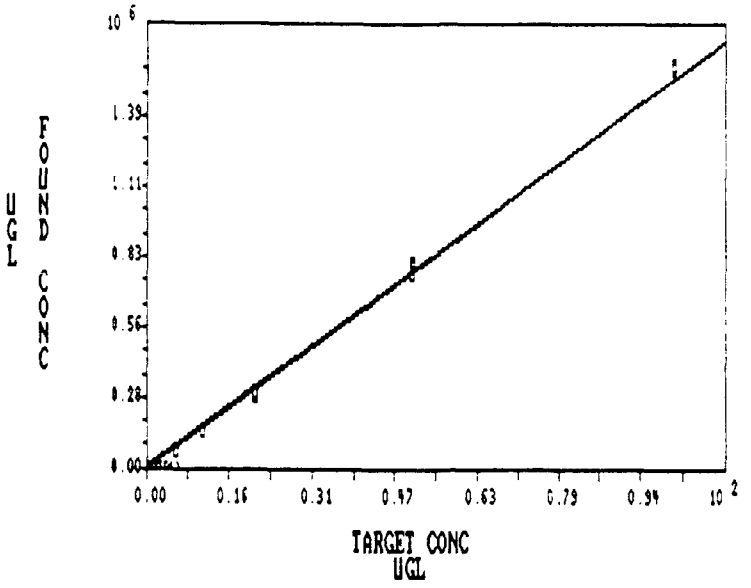

Figure 3. Spiked target concentrations versus corresponding found concentrations for MFA.

Table III. Certified Reporting Limits for Halogenated Acetic Acids Using AS5A and ICE-AS1 Columns

Halogenated Acetic Acid	CRL, mg/L	
	Columns	
	AS5A-5	ICE-AS1
BAA	1.990	5.730
CAA	1.930	3.050
MFA	1.850	0.954
ACETATE	0.985	2.680

CONCLUSIONS

An ion chromatographic method has been developed that allows halogenated organic acids to be determined in ROWPU water samples. The method developed using the inorganic anion column involves a short run time and has a lower detection limit than the method developed for using the organic acid column. However, one advantage to using the organic acid column, despite its long run time, is the excellent resolution observed on the chromatograms.

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